

**COLLISIONAL QUENCHING OF ELECTRONICALLY EXCITED CHLORINE ATOMS  $\text{Cl}((3p)^5, ^2P_{1/2})$  BY  $C_1$  CHLOROFLUOROCARBONS**

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**Summary**

A kinetic investigation of the collisional behaviour of the low-lying electronically excited chlorine atom  $\text{Cl}((3p)^5, ^2P_{1/2})$ , located  $882\text{ cm}^{-1}$  above the  $\text{Cl}((3p)^5, ^2P_{3/2})$  ground state, is reported.  $\text{Cl}(3\ ^2P_{1/2})$  was generated by the repetitive pulsed irradiation of each of the  $C_1$  chlorofluorocarbons  $\text{CF}_x\text{Cl}_{4-x}$  in a gaseous flow system kinetically equivalent to a static system and was monitored photoelectrically by time-resolved atomic resonance absorption spectroscopy in the vacuum UV at  $\lambda = 136.34\text{ nm}$  ( $\text{Cl}((3p)^4(4s), ^2P_{3/2}) \leftarrow \text{Cl}((3p)^5, ^2P_{1/2}^0)$ ) using signal averaging methods. The following absolute second-order quenching rate constants  $k_Q$  for the collisional removal of  $\text{Cl}(3\ ^2P_{1/2})$  by the freons are reported ( $k_Q$  in centimetres cubed per molecule per second; 300 K; errors,  $2\sigma$ ):  $\text{CCl}_4$ ,  $(2.1 \pm 0.6) \times 10^{-10}$ ;  $\text{CFCl}_3$ ,  $(3.1 \pm 0.6) \times 10^{-10}$ ;  $\text{CF}_2\text{Cl}_2$ ,  $(2.1 \pm 0.4) \times 10^{-10}$ ;  $\text{CF}_3\text{Cl}$ ,  $(2.2 \pm 0.4) \times 10^{-10}$ ;  $\text{CF}_4$ ,  $(1.5 \pm 0.4) \times 10^{-10}$ . These results, which are close to the unit collisional efficiencies, are compared where possible with previous measurements and estimates. This work is considered to be a basis for future work on the collisional removal of  $\text{Cl}(3\ ^2P_{1/2})$  by various gases in the polluted stratosphere.

**1. Introduction**

Investigation of the collisional behaviour of the optically metastable electronically excited chlorine atom  $\text{Cl}((3p)^5, ^2P_{1/2})$  located  $882\text{ cm}^{-1}$  above the  $\text{Cl}((3p)^5, ^2P_{3/2})$  ground state [1] is of interest from a number of viewpoints of which three can conveniently be selected. Spin-orbit relaxation and the chemistry of such an energized halogen atom is of fundamental interest [2]. Further, the production of chlorine atoms arising from the photolysis of chlorofluorocarbons (freons and arctons) and the resulting decomposition of stratospheric ozone catalysed by Cl and ClO is clearly a matter of considerable current interest in atmospheric chemistry [3 - 5]. Lastly, direct monitoring of  $\text{Cl}(3\ ^2P_{1/2})$  in a concentration above that corresponding to the Boltzmann distribution and which permits absolute collisional rate

data to be determined is a matter of experimental interest [6, 7]. This latter aspect is of special concern in this case, in contrast with the case for the heavier energized halogen species  $I((5p)^5, ^2P_{1/2})$  and  $Br((4p)^5, ^2P_{1/2})$  [2]. The Einstein coefficient  $A_{nm} = 0.012 \text{ s}^{-1}$  [2] for spontaneous emission  $Cl(3 ^2P_{1/2}) \rightarrow Cl(3 ^2P_{3/2}) + h\nu$  is far too low for monitoring the excited state for kinetic purposes and hence this lighter atomic species must be studied using an allowed electronic absorption transition in the vacuum UV [6, 7].

The collisional quenching of  $Cl(3 ^2P_{1/2})$  by freons will fall primarily but not solely in the domain of the stratospheric aspect of this investigation. The photochemical production of  $Cl(3 ^2P_{1/2})$  from all the chlorinated freons investigated here is described in this paper together with absolute collisional quenching rate constants for these photochemical precursors of which, of course,  $CFCl_3$  and  $CF_2Cl_2$  (freons 11 and 12 respectively) will be of special interest [3 - 5]. Further, the wider kinetic and stratospheric role of  $Cl(3 ^2P_{1/2})$ , given that it is generated photochemically from freons both in the laboratory and in the higher atmosphere via solar radiation, can clearly be stressed. In general the large body of collisional rate data ascribed to atomic chlorine and developed in the literature in recent years [8] does not normally differentiate between the individual roles played by the specific spin-orbit levels  $Cl(3 ^2P_{3/2})$  and  $Cl(3 ^2P_{1/2})$  primarily because the measurements from which the rate data are derived are generally made under experimental conditions in which both spin-orbit levels are in Boltzmann equilibrium. Under such conditions each spin-orbit level will demonstrate identical kinetics and a measured rate constant  $k_R$  will in fact be given by

$$k_R = \frac{k_1 + k_2K}{1 + K}$$

where  $K$  is the equilibrium constant connecting the  $^2P_{3/2}$  and  $^2P_{1/2}$  levels and  $k_1$  and  $k_2$  are respectively the true rate constants for these specific levels. Hence the absolute quenching rate data for  $Cl(3 ^2P_{1/2})$  will assist in the elucidation of the kinetic components that contribute to an effective second-order rate constant for  $Cl(3 ^2P_J)$  as normally measured. This kinetic investigation, specifically on  $Cl(3 ^2P_{1/2})$  in concentrations out of Boltzmann equilibrium, is presented against this general background of spin-orbit quenching, the role of freons in atmospheric chemistry and the effect of the collisional behaviour of both  $Cl(3 ^2P_{3/2})$  and  $Cl(3 ^2P_{1/2})$  in chlorine atom kinetics.

## 2. Experimental details

Two physical properties of atomic chlorine impose special constraints on direct experimental investigations designed to yield absolute rate data on the collisional behaviour of  $Cl(3 ^2P_{1/2})$ . One is the very low Einstein coefficient for spontaneous emission to the ground state [2] which essentially prevents either spontaneous emission or laser emission being used as a kinetic

tool in this context, and the other is the low energy splitting ( $882\text{ cm}^{-1}$  [1]). It is this latter property that has mainly restricted experimental measurements hitherto and to which brief reference is given here. Without embarking on an extensive discussion of the many factors that govern electronic energy transfer on collision, in purely empirical terms the low electronic energy to be transferred to nuclear motion with a colliding gas would be expected to be characterized by high quenching efficiencies except in the case of the light noble gases [7]. Consequently for most kinetic or spectroscopic measurements on atomic chlorine, a Boltzmann population for  $\text{Cl}(3\ ^2\text{P}_{1/2})$  corresponding to 0.7% of the total Cl population at room temperature is rapidly established. Thus, whilst this  $\ ^2\text{P}_{1/2}$  population can be monitored, for example, on a flow discharge system as described in the electron paramagnetic resonance measurements of Carrington *et al.* [9] and in the vacuum UV resonance fluorescence measurements of Clyne and Nip [10], absolute quenching rate data cannot readily be derived from the resulting signals. At present, the only practical method for determining absolute collisional rate data for  $\text{Cl}(3\ ^2\text{P}_{1/2})$  is the photochemical generation of a non-Boltzmann population of this excited state in the pulsed mode and the choice of short time scales and experimental conditions such that the excited atom is monitored before the Boltzmann equilibrium is reached. The first reported kinetic measurements on  $\text{Cl}(3\ ^2\text{P}_{1/2})$  in which this species was monitored photographically at a fixed time delay of  $10\ \mu\text{s}$  at  $\lambda = 135.17\ \text{nm}$  ( $\text{Cl}((3\text{p})^4(4\text{s})\ ^2\text{P}_{1/2}) \leftarrow \text{Cl}((3\text{p})^5, \ ^2\text{P}_{1/2}^0)$ ) following the flash photolysis of  $\text{CCl}_4$  in argon did not in fact satisfy these conditions [11]. The measurement of the spectral intensities at  $\lambda = 135.17\ \text{nm}$  with a fixed time delay in the presence of varying pressures of quenching gas assumed a first-order kinetic decay of  $\text{Cl}(3\ ^2\text{P}_{1/2})$  which was not established for the time scale of the experiment, *i.e.* within the  $10\ \mu\text{s}$  range. It is easy with hindsight resulting from the use of modern electronics in data processing [6, 7] to see that for the conditions of the early flash photolysis photographic measurements [11] ( $p_{\text{CCl}_4} = 0.02\ \text{Torr}$ ,  $p_{\text{Ar}} = 50\ \text{Torr}$  ( $1\ \text{Torr} = 133\ \text{N m}^{-2}$ ))  $\tau_e$  for collisional quenching was  $0.5\ \mu\text{s}$  from the subsequently reported collisional quenching data for  $\text{Cl}(3\ ^2\text{P}_{1/2})$  ( $k_{\text{CCl}_4} = (2.0 \pm 0.2) \times 10^{-10}$  [6];  $k_{\text{Ar}} = (1.1 \pm 0.3) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$  [7]). Hence we can only presume that the capacity to monitor photographically any  $\text{Cl}(3\ ^2\text{P}_{1/2})$  above the Boltzmann population of 0.7% resulted from measurements being made within the tail of the photoflash discharge during which time the excited atom was still being generated photochemically. Thus collisional quenching rate data resulting from the use of that method will be too low on account of the competition between photochemical production and kinetic removal of  $\text{Cl}(3\ ^2\text{P}_{1/2})$ , a matter that will be discussed later in this paper in more detail. Hence, to the best of our knowledge, the present method of time-resolved resonance absorption spectroscopy on  $\text{Cl}(3\ ^2\text{P}_{1/2})$  with photoelectric monitoring in the vacuum UV following pulsed irradiation in the repetitive mode with signal averaging and with some modifications to the earlier procedure of Fletcher and Husain [6, 7] constitutes the only general method of obtaining absolute collisional rate data directly for this spin-orbit

state. It may conceivably be the case that, notwithstanding the very low Einstein coefficient for spontaneous emission for  $\text{Cl}(3\ ^2\text{P}_{1/2}) \rightarrow \text{Cl}(3\ ^2\text{P}_{3/2}) + h\nu$  [2], this property may constitute the basis of future kinetic measurements on the  $^2\text{P}_{1/2}$  state. Davies and Russell [1] have of course now monitored  $\text{Cl}(3\ ^2\text{P}_{3/2})$  using this extremely weak transition in absorption by means of diode laser spectroscopy. Indeed, it is the high resolution of their measurement [1] that leads to the reassignment of the energy spacing of  $\text{Cl}(3\ ^2\text{P}_{1/2}) - \text{Cl}(3\ ^2\text{P}_{3/2}) = 882\ \text{cm}^{-1}$  compared with the earlier value of  $881\ \text{cm}^{-1}$  which was derived from small differences in large energy jumps associated with electronic transitions in the vacuum UV spectrum of atomic chlorine [12].

$\text{Cl}(3\ ^2\text{P}_{1/2})$  was generated by the repetitive pulsed irradiation (Spectrosil quartz,  $\lambda > 165\ \text{nm}$ ) of the appropriate chlorofluorocarbon ( $E = 180\ \text{J}$ ; repetition rate,  $0.2\ \text{Hz}$ ) in the presence of excess helium buffer gas. The collisional quenching of  $\text{Cl}(3\ ^2\text{P}_{1/2})$  by helium is sufficiently low ( $k_{\text{He}} = (3.8 \pm 0.6) \times 10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$  [6, 7]) for this noble gas to be employed as the buffer gas. Under the conditions of the present experiments, quenching of  $\text{Cl}(3\ ^2\text{P}_{1/2})$  by helium pressures in the flow system of about 15 Torr accounts for about 10% - 20% of the overall decay rate of the excited atom. This kinetic contribution was held constant in a series of experiments with varying freon concentrations by the use of a constant value of  $p_{\text{He}}$  in the total flow. As with earlier studies on  $\text{Cl}(3\ ^2\text{P}_{1/2})$  [6, 7], a coaxial lamp and vessel assembly was employed [13, 14] in an arrangement in which a slow flow system coupled with relatively rapid kinetic decays is kinetically equivalent to a static system. The excited atom was monitored photoelectrically in absorption at  $\lambda = 136.34\ \text{nm}$  ( $\text{Cl}((3\text{p})^4(4\text{s}),\ ^2\text{P}_{3/2}) \leftarrow \text{Cl}((3\text{p})^5,\ ^2\text{P}_{1/2}^0)$ ), the resonance line being derived from a microwave-powered discharge (incident power, 25 - 50 W) (EMI microwave generator type T1001) through an atomic emission spectroscopic flow lamp [15] ( $p_{\text{Cl}_2} = 2.0\ \text{N m}^{-2}$ ;  $p_{\text{He}} = 130\ \text{N m}^{-2}$ ) employing a cavity of the type described by Fehsenfeld *et al.* [16]. The photoelectric detection system differed from that used in earlier studies on  $\text{Cl}(3\ ^2\text{P}_{1/2})$  [6, 7] and, indeed, from the system used in our recent kinetic investigations of  $\text{Cl}(3\ ^2\text{P}_J)$  [17, 18]. In particular, a new solar blind photomultiplier was mounted on the exit slit of the 1 m concave grating vacuum UV monochromator (Hilger and Watts) [6, 7]. This device (Gencom G-26E315), which operates in the spectral region  $\lambda = 110 - 220\ \text{nm}$ , incorporates a CsI photocathode and an  $\text{MgF}_2$  end window (5 kV; 6 mA) (Wallis power supply) and yields a strong steady  $I_0$  signal with good signal-to-noise ratio at the wavelength of the resonance transition with an applied voltage across the tube of 2.2 - 2.4 kV which is highly suitable for time-resolved measurements of the present type [6, 7]. Furthermore the data handling system has been modified to that employed previously for the study of  $\text{Cl}(3\ ^2\text{P}_{1/2})$  [6, 7]. In these experiments, following pulsed irradiation, the resulting photoelectric signals at  $\lambda = 136.34\ \text{nm}$ , which represent the time variation of the decay of  $\text{Cl}(3\ ^2\text{P}_{1/2})$ , were amplified by means of a current-to-voltage converter employing a fast settling operational amplifier to avoid signal distur-

tion [19] and were then detected by a transient recorder (Biomation 610) interfaced to a 200-point signal averager (Data Laboratories DL 102A). The electronic procedures for initiating, summing and averaging the results of individual photoelectric decay signals on a given flowing reactant gas mixture have been given in earlier publications, as have the vacuum handling procedures with special reference to the flow system [6, 7, 13, 14]. The kinetic results for the decay of  $\text{Cl}(3^2\text{P}_{1/2})$  given in this paper generally represent the averaged result of 32 individual experiments. The contents of the signal averager were transferred onto paper tape (Data Dynamics punch 1132) in binary code for computerized analysis using the University of Cambridge IBM 370/165 computer. All materials were essentially prepared as described by Fletcher and Husain [20] in their study of the collisional behaviour of  $\text{O}(2^1\text{D}_2)$  with the halogenated paraffins using resonance line absorption at  $\lambda = 115.2 \text{ nm}$  ( $\text{O}(3^1\text{D}_2^0) \leftarrow \text{O}(2^1\text{D}_2)$ ).

### 3. Results and discussion

Previous kinetic measurements on  $\text{Cl}(3^2\text{P}_{1/2})$  using time-resolved atomic resonance absorption spectroscopy following pulsed irradiation, and leading to absolute rate constants for collisional quenching by a number of gases [6, 7], employed  $\text{CCl}_4$  as the photochemical source. Despite the high efficiency for the collisional quenching of  $\text{Cl}(3^2\text{P}_{1/2})$  exhibited by this molecule [6, 7] (see later), this is a particularly convenient precursor for the generation of the excited atomic state using UV radiation (refs. 6 and 7 and this work) as seen from the degrees of resonance absorption, and hence this gas is normally the basis for collisional quenching studies by added gases. However, in the present investigation each chlorofluorocarbon was employed as its own photochemical source of  $\text{Cl}(3^2\text{P}_{1/2})$ . Thus we see immediately that the excited chlorine atom is generated from the UV photolysis of the two stratospherically important freons  $\text{CFCl}_3$  and  $\text{CF}_2\text{Cl}_2$ . We restrict detailed description of the photochemical production of  $\text{Cl}(3^2\text{P}_{1/2})$  here to  $\text{CFCl}_3$  as an example, as that for  $\text{CCl}_4$  has been given in earlier studies [6, 7]. In general terms the photochemical yields of  $\text{Cl}(3^2\text{P}_{1/2})$  increase with the number of chlorine atoms in  $\text{CF}_x\text{Cl}_{4-x}$ . For the quenching of  $\text{Cl}(3^2\text{P}_{1/2})$  by  $\text{CF}_4$ ,  $\text{CCl}_4$  was employed as the source of atomic chlorine.

Figure 1 shows the digitized time variation of the transmitted light intensity at  $\lambda = 136.34 \text{ nm}$  ( $\text{Cl}((3\text{p})^4(4\text{s}), ^2\text{P}_{3/2}) \rightarrow \text{Cl}((3\text{p})^5, ^2\text{P}_{1/2}^0)$ ), indicating the decay of resonance absorption by  $\text{Cl}(3^2\text{P}_{1/2})$  following the pulsed irradiation of  $\text{CFCl}_3$  at two different precursor pressures in the presence of a helium buffer gas. Unlike previous measurements using  $\text{CCl}_4$  [6, 7], first-order kinetic plots (*i.e.*  $\ln\{\ln(I_0/I_{\text{tr}})\}_t$  ( $\lambda = 136.34 \text{ nm}$ ) *versus*  $t$ ) were not immediately constructed from these decay signals. This is on account of the loss in accuracy resulting from the relatively large errors in the logarithmic plots at low degrees of resonance light absorption and the further reduction in accuracy in this system which employs a 200-point signal averager (see

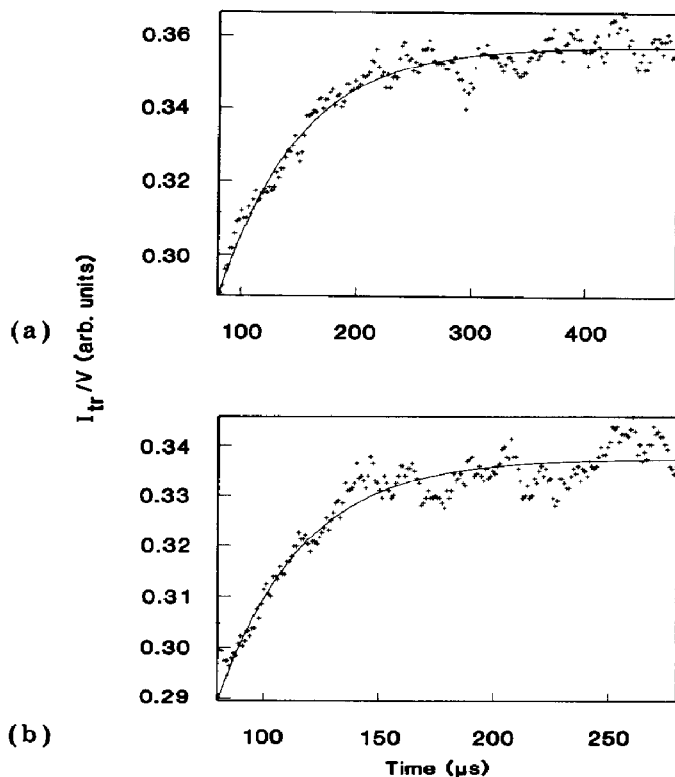


Fig. 1. Digitized time variation of the transmitted light intensity  $I_{tr}$  at  $\lambda = 136.34$  nm ( $\text{Cl}((3p)^4(4s), ^2P_{3/2}) \rightarrow \text{Cl}((3p)^5, ^2P_{1/2}^0)$ ) indicating the decay of resonance absorption by  $\text{Cl}(3\ ^2P_{1/2})$  following the pulsed irradiation of  $\text{CFCl}_3$  in the presence of helium (+, digitized data points; —, computerized fitting of raw data to the form  $I_{tr} = I_0 \exp[-A \times \{\exp(-k't)\}]$ ): (a)  $p_{\text{CFCl}_3} = 0.107$  N m $^{-2}$  (sweep rate, 2  $\mu\text{s}$  per channel); (b)  $p_{\text{CFCl}_3} = 0.327$  N m $^{-2}$  (sweep rate, 1  $\mu\text{s}$  per channel).  $E = 180$  J;  $p_{\text{total with He}} \approx 1.9$  kN m $^{-2}$ ; repetition rate, 0.2 Hz; average of 32 individual experiments.

Section 2) in contrast with the 1024-point memory of the signal averager employed hitherto [6, 7]. All measurements of the present type, including this one, are subject to the loss of the early part of the decay signal, which unfortunately would correspond to the largest degree of resonance absorption, because of the effect of scattered light. This limits the shortest time scale that can be employed on the signal averager. The limit to the longest time scale that can be used is determined both by the lowest pressure of the freon commensurate with measurable degrees of resonance absorption following photolysis and the effect of diffusion due to  $\text{Cl}(3\ ^2P_j)$  on the computed and measured  $I_0$  signal (see later). The first of these limitations is particularly aggravated in the study of rapid decays of the quenching of  $\text{Cl}(3\ ^2P_{1/2})$  by freons. The overall first-order decay coefficient  $k'$  for the removal of  $\text{Cl}(3\ ^2P_{1/2})$  in an individual experiment was therefore derived from plots of the type given in Fig. 1 for the various freons investigated which were obtained by computerized fitting to the form  $I_{tr} = I_0 \exp[-A \times \{\exp(-k't)\}]$  using a standard NAGLIB routine. The full curves in Fig. 1

show the result of the fitting procedure. The scatter in the raw data arises essentially from the limited number of data points, the effect of scattered light at short times, the fast decays necessarily investigated using freon pressures that gave rise to resonance absorption signals of suitable magnitude and finally to the production of colour centres in the LiF optical materials which reduce the  $I_0$  signal.

The meaning of  $I_0$  ( $\lambda = 136.34$  nm) in the fitted form requires fundamental consideration in the present circumstances. For a resonance absorption law, be it the Beer-Lambert law or a modified law (*e.g.*  $I_{tr} = I_0 \times \exp\{-(\epsilon cl)^\gamma\}$  [21]),  $I_0$  is normally the magnitude of the incident spectroscopic signal at the resonance transition unattenuated by transient atoms. It is thus usually determined experimentally either by direct measurement prior to photolysis or at infinite time when the transient atom generated on pulsed photolysis has been removed by kinetic processes. It cannot be determined in this way in the present measurements by virtue of the Boltzmann distribution in  $\text{Cl}(3^2\text{P}_{1/2})$  which accounts for 0.7% of atomic chlorine at 300 K. Two kinetic regimes can be envisaged for  $\text{Cl}(3^2\text{P}_{1/2})$ , the first yielding rapid relaxation to a Boltzmann distribution for atomic chlorine and the second slower process resulting from the overall removal of  $\text{Cl}(3^2\text{P}_J)$ , the  $^2\text{P}_{1/2}$  and  $^2\text{P}_{3/2}$  states being linked kinetically (see Section 1). This can readily be seen in experiments of the present type by inspection of decays at short and long times. The  $I_0$  signal for the first regime is thus not attainable by the standard methods and can only be determined by curve fitting, as described. Hence in the curve fitting procedure  $I_0$  represents the transmitted light intensity at the Boltzmann equilibrium;  $A$  is directly proportional to the difference between the initial and equilibrium concentrations of  $\text{Cl}(3^2\text{P}_{1/2})$ . A standard first-order kinetic scheme for competing reactions demonstrates this. It is necessary to determine  $I_0$  for the fast decay regime for the kinetic analysis; it is of course  $k'$  that is finally the object of kinetic interest in these investigations.

In view of the large magnitude of the quenching rate constants for the freons in general, and  $\text{CFCl}_3$  as the particular example described, necessitating the use of low pressures of the materials, the standard procedure used for the determination of  $\gamma$  in the modified Beer-Lambert law [21] was used here in reverse as a test of the initial concentration of the photochemical source. This test was particularly influenced by various minor experimental effects including dilution processes which indicate that special care must be taken to ensure quantitative control of the concentration of the chloro-fluorocarbons admitted to the reaction vessel at the millitorr level. A continuous flow system of the kind employed here minimizes the effect on the kinetics of  $\text{Cl}(3^2\text{P}_{1/2})$  resulting from absorption of the photochemical precursor onto that part of the vacuum system involved in the flow, including the reaction vessel itself. A conventional investigation of  $\gamma$  was not undertaken here. As in previous measurements on time-resolved resonance absorption by  $\text{Cl}(3^2\text{P}_{1/2})$  [6, 7], the Beer-Lambert law was assumed to hold for the  $\lambda = 136.34$  nm transition (*i.e.*  $\gamma$  is unity). A fundamental assumption

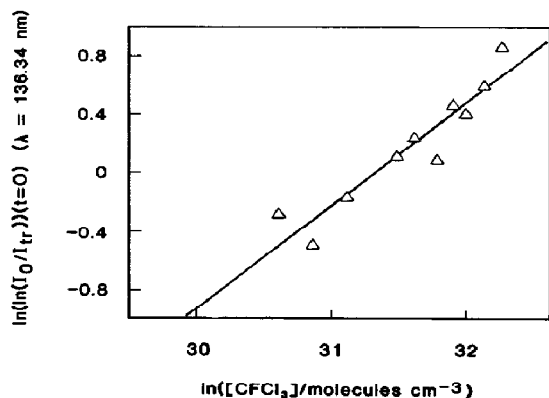


Fig. 2. Plot of  $\ln\{\ln(I_0/I_{tr})\}(t=0)$  ( $\lambda = 136.34$  nm;  $\text{Cl}((3p)^4(4s), {}^2P_{3/2}) \rightarrow \text{Cl}((3p)^5, {}^2P_{1/2}^0)$ ) against  $\ln[\text{CFCl}_3]$  derived from the extrapolation of first-order decay measurements on  $\text{Cl}(3 {}^2P_{1/2})$  following the pulsed irradiation of  $\text{CFCl}_3$  ( $E = 180$  J;  $P_{\text{total}}$  with He  $\approx 1.9$  kN m $^{-2}$ ).

in the standard determination of  $\gamma$  is that of linearity in the relationship between the initial transient atomic concentration and the concentration of the precursor [21] (in this case  $[\text{Cl}(3 {}^2P_{1/2})](t=0) \propto [\text{CFCl}_3](\text{initial})$ ). Hence the value of  $\ln\{\ln(I_0/I_{tr})\}(t=0)$  at  $\lambda = 136.34$  nm, which involved the use of the computerized value of  $I_0$  indicated above, is a linear measure of  $\ln[\text{Cl}(3 {}^2P_{1/2})](t=0)$  which is in turn a linear measure of  $\ln[\text{CFCl}_3](\text{initial})$ . The values of  $\ln\{\ln(I_0/I_{tr})\}(t=0)$  (the above parameter  $\ln A$ ) are automatically generated in the computerized analysis. Figure 2 shows the plot of  $\ln\{\ln(I_0/I_{tr})\}(t=0)$  versus  $\ln[\text{CFCl}_3]$ . Were this a standard investigation of  $\gamma$ , the slope of this plot yields  $\gamma = 0.9 \pm 0.1$ , *i.e.* unity within experimental error. By the same token and for the reasons given above this plot demonstrates that, within the scatter of the experimental data, the relative values of  $[\text{CFCl}_3]$  employed in the various kinetic runs calculated from the flow calibrations do reach the photochemical reactor under the conditions of flow.

$k'$  derived from computerized fitting of the type shown in Fig. 1 was taken to be described by the form

$$k' = K + k_{\text{CFCl}_3}[\text{CFCl}_3] \quad (1)$$

for the particular case of freon 11.  $K$  is a constant for a series of kinetic runs in which the pressure of the helium buffer gas in the total flow is maintained at a sensible constant rate and  $k_{\text{CFCl}_3}$  is the absolute second-order quenching rate constant for the removal of  $\text{Cl}(3 {}^2P_{1/2})$  by  $\text{CFCl}_3$ . Similar analyses were performed for the other chlorinated fluorocarbons. Hence we can plot  $k'$  versus  $[\text{CFCl}_3]$  or  $k' - K$  versus  $[\text{CFCl}_3]$  to determine  $k_{\text{CFCl}_3}$ . Figure 3 shows plots of the form of eqn. (1) for the removal of  $\text{Cl}(3 {}^2P_{1/2})$  by  $\text{CFCl}_3$  and also by  $\text{CCl}_4$  for comparison with previous work. Figure 4 shows the analogous pair of plots for the stratospheric pollutant  $\text{CF}_2\text{Cl}_2$  and for  $\text{CF}_3\text{Cl}$ . Finally, the collisional quenching of  $\text{Cl}(3 {}^2P_{1/2})$  by  $\text{CF}_4$  was investigated by monitoring the decay of the excited atom using a fixed concentration of  $\text{CCl}_4$  and a



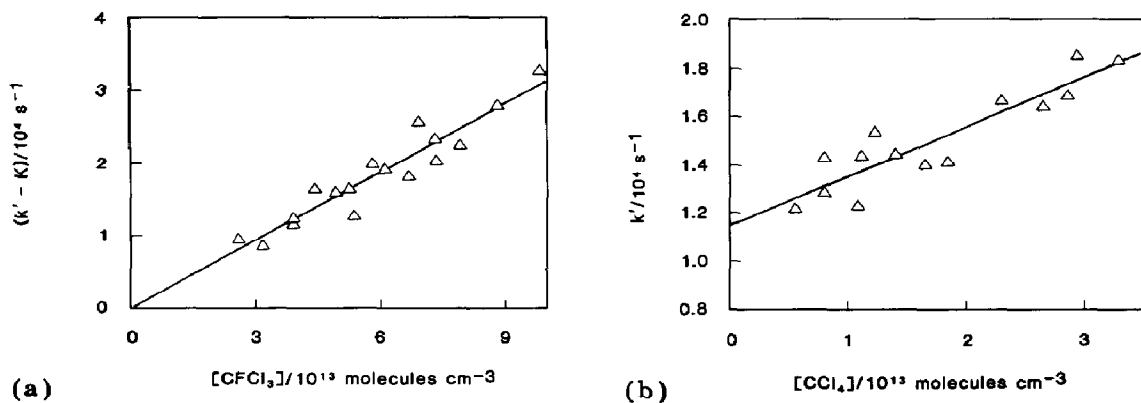


Fig. 3. Plots of pseudo-first-order rate coefficients for the decay of  $\text{Cl}(3^2\text{P}_{1/2})$  in the presence of (a)  $\text{CFCl}_3$  ( $k' - K$ ) and (b)  $\text{CCl}_4$  ( $k'$ ) ( $p_{\text{total}}$  with He  $\approx 1.9 \text{ kN m}^{-2}$ ).

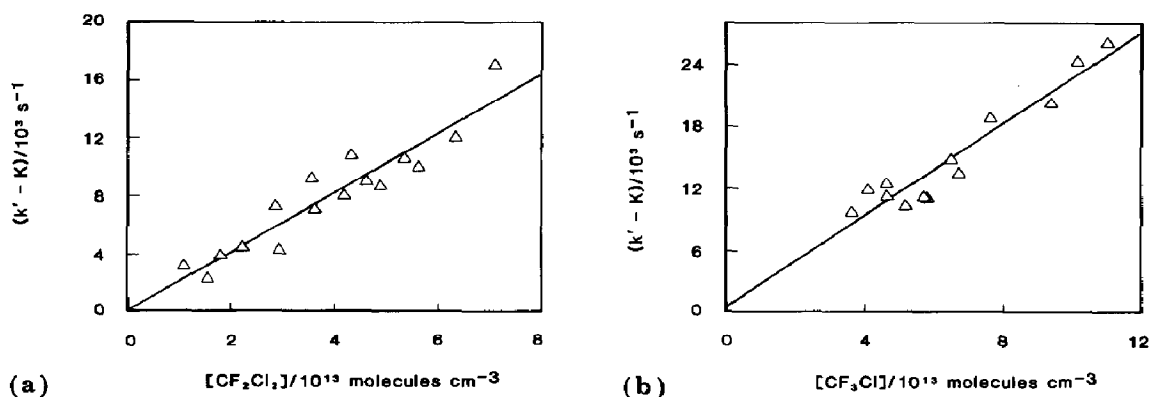


Fig. 4. Plots of pseudo-first-order rate coefficients  $k' - K$  for the decay of  $\text{Cl}(3^2\text{P}_{1/2})$  in the presence of (a)  $\text{CF}_2\text{Cl}_2$  and (b)  $\text{CF}_3\text{Cl}$  ( $p_{\text{total}}$  with He  $\approx 1.9 \text{ kN m}^{-2}$ ).

fixed helium pressure. The plot analogous to eqn. (1), with the contribution to  $k'$  from the term  $k_{\text{CCl}_4}[\text{CCl}_4]$  being held constant in this series of measurements, is shown in Fig. 5. Absolute values for the quenching rate constants  $k_{\text{Q}}$  for the molecules  $\text{CF}_x\text{Cl}_{4-x}$  were thus obtained from the slopes of the appropriate plots in Figs. 3 - 5, and the results are presented in Table 1 together with values obtained from previous investigations.

Before the magnitudes of  $k_{\text{Q}}$  are discussed, we see from Table 1 that there is good agreement between the value of  $k_{\text{CCl}_4}$  obtained in the present investigation with that obtained previously using time-resolved resonance absorption spectroscopy [6]. The low value of  $k_{\text{CCl}_4}$ , and also that for  $k_{\text{CF}_3\text{Cl}}$  derived from plate photometric measurements [11], can clearly be ascribed to the rapid establishment of a Boltzmann equilibrium between  $\text{Cl}(3^2\text{P}_{1/2})$  and  $\text{Cl}(3^2\text{P}_{3/2})$  using argon as the buffer gas (see Section 2). The quoted errors are equal to  $2\sigma$  and are derived from the plots given in Figs. 3 - 5. All the quenching constants show values in the region of the collision numbers

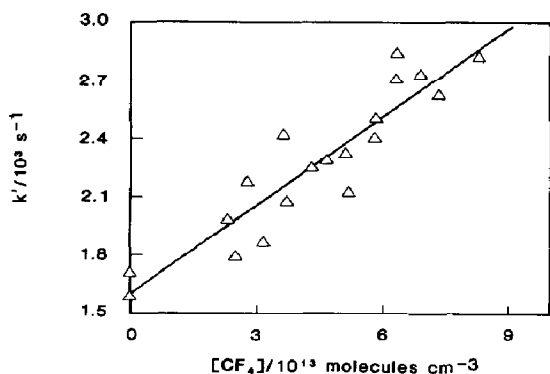


Fig. 5. Plot of pseudo-first-order rate coefficients  $k'$  for the decay of  $\text{Cl}(3^2\text{P}_{1/2})$  in the presence of  $\text{CF}_4$  ( $p_{\text{CCl}_4} = 0.16 \text{ N m}^{-2}$ ;  $p_{\text{total with He}} \approx 1.9 \text{ kN m}^{-2}$ ).

TABLE 1

Absolute second-order rate constants  $k_{\text{Q}}$  for the collisional removal of electronically excited chlorine atoms  $\text{Cl}(3^2\text{P}_{1/2})$  by  $\text{C}_1$  chlorofluorocarbons

Quenching gas	$k_{\text{Q}}^{\text{a}}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	Reference
$\text{CCl}_4$	$(2.1 \pm 0.4) \times 10^{-10}$	This work
	$(2.0 \pm 0.2) \times 10^{-10}$	[6]
	$5 \times 10^{-11}$	[11]
$\text{CFCl}_3$	$(3.1 \pm 0.6) \times 10^{-10}$	This work
$\text{CF}_2\text{Cl}_2$	$(2.1 \pm 0.4) \times 10^{-10}$	This work
$\text{CF}_3\text{Cl}$	$(2.2 \pm 0.4) \times 10^{-10}$	This work
	$2.5 \times 10^{-13}$	[11]
$\text{CF}_4$	$(1.5 \pm 0.4) \times 10^{-10}$	This work

<sup>a</sup>Measured at 300 K; error,  $2\sigma$ .

which themselves merit brief consideration. As examples, the Lennard-Jones  $\sigma$  values for  $\text{CCl}_4$  and  $\text{CF}_4$  of 5.8 Å and 4.7 Å respectively (1 nm = 10 Å) [22] coupled with the van der Waals radius of atomic chlorine of 1.8 Å [23] yield collision numbers for  $\text{Cl} + \text{CCl}_4$  and  $\text{Cl} + \text{CF}_4$  of  $3.2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  respectively at 300 K. The measured diffusion coefficient for  $\text{Cl}(3^2\text{P}_{1/2})$  in helium reported by André *et al.* [17] ( $D_{12} = 0.43 \text{ cm}^2 \text{ s}^{-1}$  at 1 atm and 300 K) together with simple gas kinetic theory [24], a Lennard-Jones value for  $\sigma_{\text{He}}$  of 2.6 Å [22] and the standard additivity mean rule for  $\sigma$  yields a van der Waals radius for Cl of 2.6 Å and collision numbers which are correspondingly larger than those given above.

In our view detailed consideration of electronic-to-vibrational energy transfer between  $\text{Cl}(3^2\text{P}_{1/2})$  and the quenching molecules considered here is not particularly useful in view of the small electronic energy to be transferred. The molecules listed in Table 1 possess fundamental frequencies within about  $100 \text{ cm}^{-1}$  or less of that of  $\Delta E(2^2\text{P}_{1/2-3/2})$  [25 - 29] and this, coupled

with the effects of rotational and translational excitation and also the chemical interaction, readily accounts for the high collisional quenching efficiencies demonstrated by the C<sub>1</sub> chlorofluorocarbons.

The present investigations provide the basis for detailed measurements of the collisional removal of Cl(3 <sup>2</sup>P<sub>1/2</sub>) by atmospheric gases. This work has demonstrated that the electronically excited chlorine atom is generated by the photolysis of the chlorine-containing C<sub>1</sub> freons followed by collisional quenching at rates in the region of the collision numbers. The kinetic contribution to the overall removal of Cl(3 <sup>2</sup>P<sub>1/2</sub>) by atmospheric gases in the stratosphere will of course be determined by the particle density of each gas. Altitude profiles in the stratosphere for species such as CF<sub>2</sub>Cl<sub>2</sub> and CFCl<sub>3</sub> indicate low volume mixing ratios (*e.g.* in the range 10<sup>-12</sup> - 10<sup>-10</sup>) for these species [4, 30] and thus, notwithstanding the collision efficiency of almost unity for the removal of Cl(3 <sup>2</sup>P<sub>1/2</sub>) by the freons themselves, overall removal will primarily be governed by the atmospheric gases. Fletcher and Husain [6] have reported  $k_{O_2} = (2.1 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (300 K), *i.e.* a collisional efficiency of about 0.1, and to the best of our knowledge this gas is the only simple atmospheric gas whose collisional behaviour with Cl(3 <sup>2</sup>P<sub>1/2</sub>) has been investigated in detail. The removal of the excited atom by the atmospheric gases is currently being studied.

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